



# An overview of the methylene blue ISO test for assessing the activities of photocatalytic films

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## ABSTRACT

The main features are described of the ISO published standard: 10678:2010, namely the 'Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue'. The main underlying assumptions of the standard are considered, namely: (i) dye purity, (ii) adsorption and pH, (iii) light source, (iv) stirring and diffusion, (v) reaction mechanism and (vi) kinetics. Possible sources of errors arising from these assumptions are identified and changes to the standard's protocol suggested. The major suggested changes are: (i) a source of MB<sup>+</sup> of known and proven on site high purity (>90%) should be used to make up the standard test solution, which should have a referenced absorbance, 0.74, at 665 nm; (ii) the conditioning solution should be the same concentration as the standard test solution, (iii) the initial pH of the reaction solution should lie in the range: 5.5–6.0; (iv) a BLB UVA light with a europium-doped strontium fluoroborate or borate phosphor should be used; (v) the reaction solution should be vigorously and continuously stirred if possible; (vi) the solution height should be the minimum recommended value of 2 cm, and the photoreactor cylinder i.d., 4.7 cm; (vii) after the 3 h irradiation the reaction solution should be left stirring overnight to check that no dye photoreductive bleaching has occurred. Application of most of these suggestions should improve considerably the standard's reported current poor percentage errors for repeatability within a lab (9.2%) and reproducibility between labs (30.6%).

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## 1. Introduction

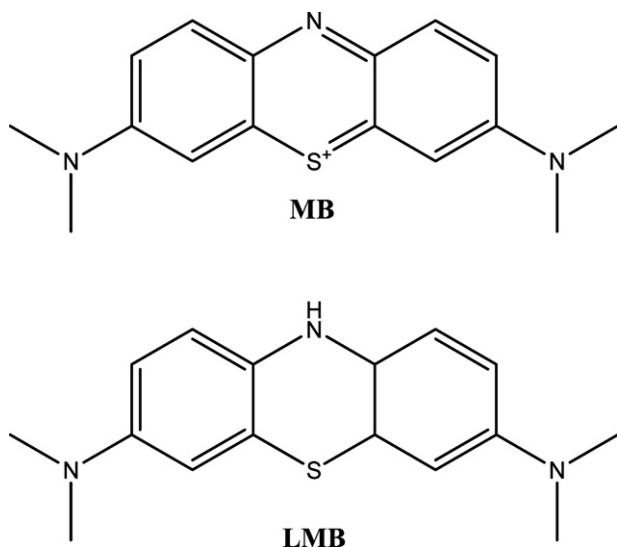
The ISO (International Organization for Standardization) is the world's leading developer and publisher of international standards, comprising a network of the national standards institutes of 162 countries, with a central co-ordinating secretariat in Geneva, Switzerland [1]. The ISO is a non-governmental organisation that bridges the public and private sectors and so is able to generate consensual standards that meet the requirements of both business and society. In 2010 the ISO published standard: 10678:2010, namely the 'Determination of photocatalytic activity of surfaces in an aqueous medium by degradation of methylene blue' [2]. Given the continuing popularity of the methylene blue test in photocatalysis [3] and that the standard is up for review in 2013, it appears useful to examine in detail the background and key details of the ISO standard and identify the underlying assumptions and any possible improvements.

Looking at the stated purpose of this particular standard, it is not readily apparent why it is particularly appropriate for evaluating 'the specific self-cleaning activity of surfaces', rather than, say, for assessing the ability of such films to degrade dissolved organic

molecules as part of their potential use in water remediation. However, this is probably a moot point, since the standard, which is clearly based on water remediation and not surface cleaning, will provide a measure of activity of the coating which will most likely be closely related to its ability to clean its surface of deposited organic species.

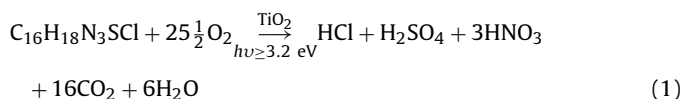
In terms of water remediation, it can be argued that there is no greater demonstration of the efficacy of a photocatalyst for this purpose than the *observed* destruction of a pollutant. It follows that to effect such a demonstration a dye should be used as the test pollutant, since only a small amount of material will be needed to bring about a striking colour change as the dye is photo-oxidised. It also seems reasonable to use a dye as a test pollutant since dyes from the dye industry are a recognised source of pollution. Indeed, it is estimated ca. 15% of the total production of colourants is lost during their synthesis and production and the degree of pollution they cause is significant, since ca. 0.9 million tonnes of organic dyes are produced annually [4]. The biggest selling dye is indigo, followed by various azo dyes such as: reactive black 5 and disperse blue 79. However, the dye chosen in this ISO test is much less widely used as a material dye; methylene blue, MB<sup>+</sup>, is a thiazine dye, also called basic blue 9, which finds many applications, including as a textile dye. Fig. 1 illustrates the structure of MB<sup>+</sup> and its colourless, reduced form leuco-methylene blue, LMB.

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**Fig. 1.** Structures of methylene blue, MB<sup>+</sup>, and its colourless, reduced form, leuco-methylene blue, LMB.

The current popular use of MB<sup>+</sup> as a test pollutant in semiconductor photocatalysis most probably stems from its very early application in the field in this role, in which it proved excellent at highlighting the efficacy of the photocatalytic process for removing water pollutants. Thus, as early as 1989 Matthews [5] showed that films of titania were able to mediate the complete photomineralisation of MB<sup>+</sup> (C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl).

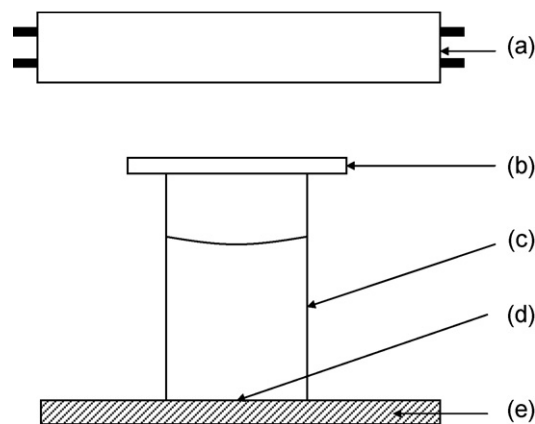


Following on from this work [5], many researchers have used MB<sup>+</sup> as a test reagent to probe the effectiveness of their reactors, light sources, catalysts and photocatalysts. Indeed, a search of the literature using the key words 'TiO<sub>2</sub> and methylene blue' reveals 1726 citations, with Matthew's work the first of these.

High on the list of key features which makes MB<sup>+</sup> so attractive as a test dye pollutant is its large molar absorptivity; brief examination of the literature reveals values ranging from: (4.0 to 9.5) × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> at λ<sub>max</sub> = 665 nm, vide infra [6–13]. This feature permits a dramatic colour change, from blue to colourless, to be effected when the dye's conjugation is broken by the photo-oxidative process and so provides a striking visual demonstration of the efficacy of the photocatalytic system under test. The high molar absorptivity of MB<sup>+</sup> also allows for the ready measurement of the rate of photobleaching effected by a semiconductor photocatalyst (film or power) via UV/vis spectrophotometry, the technique used in the ISO standard.

Another attractive feature of MB<sup>+</sup> is its largely non-toxic nature as evidenced by the fact that it can be taken orally (as in the treatment of malaria) and intravenously (as in the treatment of cyanide poisoning) with no apparent adverse long-lasting side effects. It also has a high solubility in water, ca. 50 g dm<sup>-3</sup>; which makes it easy to dissolve and to make the usually low concentration solutions (10<sup>-5</sup> M in the ISO test for example) used in most photocatalyst-sensitised, dye photobleaching experiments.

MB<sup>+</sup> is also usually very stable in aqueous solution, although it is worth noting it has a pK<sub>a</sub> = 0 and, in addition, above pH 9 it is increasingly prone to decomposition via hydrolysis to form methylene violet Berntsen (λ<sub>max</sub> = 520 nm) which has a low solubility in water (0.6 g dm<sup>-3</sup>) [14]. The latter reaction is usually



**Fig. 2.** Schematic illustration of the MB<sup>+</sup> ISO standard's suggested main photoreactor system (Annex B1), comprising: (a) a UVA light source, (b) a pane of glass (presumably to minimise contamination), (c) a cylinder of glass, glued to the sample to create a test area (d) of the sample under test (e).

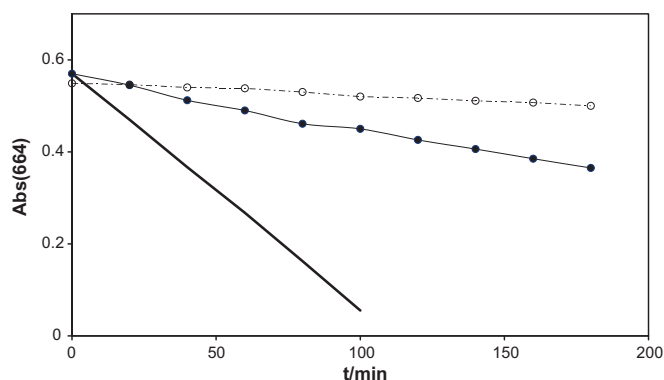
of little concern in most photocatalytic experiments involving the photomineralisation of MB<sup>+</sup> since they are conducted in neutral or mildly acidic solution. In addition, as such irradiations proceed, unless buffered, the solution becomes increasingly acidic due to the production of carboxylic and sulphonic acid intermediate species and eventually the mineral acids HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, via reaction (1) [5].

Finally, in addition to its many other applications, MB<sup>+</sup> is still used, albeit no longer on a large scale, as a textile, leather and paper dye and so is not an unreasonable choice as a test pollutant dye for the photocatalytic remediation of water, although maybe not quite as obvious a test pollutant for assessing self-cleaning films.

## 2. The standard

Most of the standard's text and the example results given are for the photoreaction system illustrated in Fig. 2, comprising a sample (with active coating) plate (typically, 10 cm square) onto which is fixed (usually with a silicone sealant—although this is not specified) a glass cylinder (3–4.7 cm diameter). Into the cylinder of this sample plate-cylinder combination is first placed 35 ml of a 'conditioning' solution of 2 × 10<sup>-5</sup> M MB<sup>+</sup> (made up using the commonly available trihydrate chloride salt of MB<sup>+</sup>; MW: 373.90) for 12 h in the dark. If, after this period, the [MB<sup>+</sup>] is <10<sup>-5</sup> M the conditioning step must be repeated using a fresh conditioning step. If this is not the case, then 35 ml of a 10<sup>-5</sup> M MB<sup>+</sup> solution are added and the cylinder covered with a UV transparent glass pane – presumably made of quartz or borosilicate. The system is then irradiated with UVA light (1.0 mW m<sup>-2</sup>; the irradiance being measured with a spectroradiometer) from a narrow-band emitter, such as a black-light blue (BLB) lamp (although it is not specified). The reaction solution is agitated (by manual stirring, magnetic stirrer flea or air sparging) every 20 min. The variation in the concentration of the methylene blue as a function of irradiation time is measured spectrophotometrically either directly (through the test solution) or by sampling the solution and returning the sample after the measurement of the solution's absorbance at 664 nm. The irradiation process is carried out for 3 h or anytime less if the solution is decolourised sooner. The reaction temperature should be 23 ± 2 °C. A blank (dark) experiment is then run. A typical set of data are illustrated in Fig. 3, from which the photonic efficiency of the system can be calculated, ξ<sub>MB</sub> = 100 × rate of MB<sup>+</sup> photobleaching (units: molecules/cm<sup>2</sup>/s)/irradiance (units: number of photons/cm<sup>2</sup>/s).

The standard's protocol notes that if ξ<sub>MB</sub> is >0.1%, the experiment should be repeated but with an irradiance of 0.25 mW/cm<sup>2</sup> and a



**Fig. 3.** Typical data reported for the MB<sup>+</sup> ISO standard (Annex A) recorded: (i) in the absence (○) and (ii) presence (●) of 1 mW/cm<sup>2</sup> of UVA light, from which data a value for the mean photonic efficiency was determined as 0.024%. The thick solid line illustrates the photobleaching decay profile which would be expected for a system that functioned at the upper limit of the reliability of this test, i.e.  $\xi_{\text{MB}} = 0.1\%$ .

new value for the photonic efficiency ( $\xi_{\text{MB}'}$ ) should be calculated. If  $\xi_{\text{MB}'} > \xi_{\text{MB}}$ , then the former value should be used and both values reported.

Finally, there is an alternative measuring device given in this standard, in which both a sample and blank sample are placed in stirred beakers containing the MB<sup>+</sup> solution and test samples and irradiated from above and monitored continuously via UV/vis spectrophotometry.

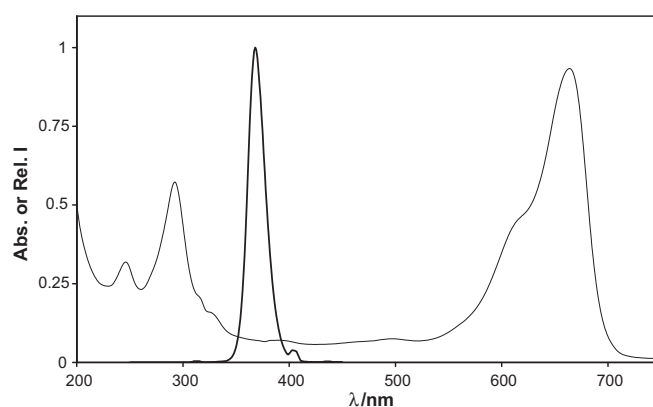
### 3. Test assumptions

The main advantage of this assessment method is its apparent simplicity. Unfortunately, this apparent simplicity is based on a number of assumptions, many of which are, or could be under certain conditions, invalid. Obviously to appreciate the results of any test and their inherent reliability it is necessary to understand any underlying assumptions. The major assumptions are as follows:

#### 3.1. Dye purity

The ISO standard not unreasonably perhaps assumes that the methylene blue used is of a high purity, quoting a molar absorptivity of  $7.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 664/5 nm ( $\epsilon_{\text{MB}}$ ) [15]. However, Table 1 lists some of the different values for  $\epsilon_{\text{MB}}$  quoted in the literature and the variation is surprisingly large, i.e.  $(4.0\text{--}9.5) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . Clearly this variance is a reflection of the purity of commercial sources of methylene blue, as has been noted by others [7] and although there are reported procedures for purifying MB<sup>+</sup> [14,16], they are often very time-consuming and low-yielding. The impurities are most likely other thiazine dyes, such as azure B, and inorganic salts. As an aside, it is interesting to note that in the ISO standard the example absorbance data given for the  $10^{-5} \text{ M}$  MB<sup>+</sup> solution in the blank and illuminated solutions at  $t=0$  are 0.55 and 0.57, respectively, see Fig. 3, implying a molar absorptivity of  $(5.5\text{--}5.7) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for the  $10^{-5} \text{ M}$  MB<sup>+</sup> test solution, i.e. very much below the value of  $7.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  cited in the standard itself [15].

In order to minimise concerns regarding the effect of dye impurities on the kinetics of MB<sup>+</sup> photobleaching it is important to identify and self-validate (by measuring its value of  $\epsilon_{\text{MB}}$ ) a high (>90%) purity commercial source of MB<sup>+</sup>, such as that provided by Aldrich Chemicals. In fact, dye purity is a bigger problem than at first it might seem as the kinetics of MB<sup>+</sup> photobleaching are highly dependent in a non-linear fashion upon [MB<sup>+</sup>] as described further in Section 3.5 [17], thus, all things being identical, the standard will generate different values for  $\xi_{\text{MB}}$  if different purities of MB<sup>+</sup> are used.



**Fig. 4.** UV/visible absorbance spectrum of a  $10^{-5} \text{ M}$  solution of MB<sup>+</sup> (thin solid line) and relative emission spectrum of a 8 W BLB with a europium-doped strontium fluoroborate or borate phosphor.

#### 3.2. Adsorption and pH

At solution pH values below the point of zero charge of the semiconductor (ca. pH 6.6 for TiO<sub>2</sub>) the adsorption of MB<sup>+</sup> via coulombic attraction is likely to be negligible [18]. Interestingly, in the MB<sup>+</sup> ISO standard the pH of the reaction solution is not stipulated, although water is used as the solvent and so should be between pH 5 and 8 [19]. It is thus assumed that the pH of the reaction solution will be the same from lab to lab and that the amount of dye adsorbed is small and/or reproducible. In order to approach this ideal, the initial pH of the reaction solution needs to be defined in the ISO standard and a pH in the range 5.5–6.0 appears appropriate and easily achieved. Note that as the photocatalysed reaction (1) proceeds, the pH of the reaction solution will drop, as various acidic species are generated, eventually reaching ca. pH 4.3 (corresponding to an acid concentration of  $5 \times 10^{-5} \text{ M}$ , i.e. five times that of the initial MB<sup>+</sup> concentration) [5].

It is not clear why a 'conditioning solution', i.e. a pre-reaction solution for pre-adsorbing the MB<sup>+</sup> onto the surface of the semiconductor film, of  $2 \times 10^{-5} \text{ M}$  MB<sup>+</sup> is used, rather than the same concentration of the reaction solution itself, i.e.  $10^{-5} \text{ M}$  MB<sup>+</sup>. The latter appears more appropriate given the test and will be less prone to error caused by dye desorption caused by the introduction of a conditioned sample to a reaction solution of a concentration that is less than the conditioning solution.

#### 3.3. Light source

The ISO standard suggests a narrow-band emitter, in the range 320–400 nm, i.e. a UVA light source, should be used with an irradiance of  $1 \text{ mW/cm}^2$ , as measured at the height of the sample underneath the covering glass pane (see Fig. 2). However, since there are many different UVA light sources and manufacturers of such, this appears to be too poorly defined and likely to cause a significant variation in the results generated using the same sample, but in different laboratories. The nature of the light source needs to be much better defined and it is suggested here that a reasonable approach is to employ the common black light blue (BLB) fluorescent tube as the light source. In particular, this BLB lamp should have a europium-doped strontium fluoroborate or borate phosphor, which generates an emission peak at ca. 365 nm with a 20 nm bandwidth (see Fig. 4); such lamps are manufactured by Osram for example [20].

**Table 1**  
Different  $\epsilon_{\text{MB}}$  for MB<sup>+</sup>.

Molar absorptivity ( $\epsilon_{\text{MB}}$ ) at 665 nm/(M <sup>-1</sup> cm <sup>-1</sup> )	Ref.	Molar absorptivity ( $\epsilon_{\text{MB}}$ ) at 665 nm/(M <sup>-1</sup> cm <sup>-1</sup> )	Ref.
40,000	[6]	71,800	[10]
54,000	[7]	82,000	[11]
58,300	[8]	84,000	[12]
64,000	[9]	95,000	[13]

### 3.4. Stirring and diffusion

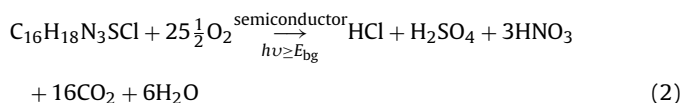
The ISO standard assumes that the reaction kinetics for reaction (1) are activation, rather than diffusion controlled, as evidenced by the standard's recommended token degree of stirring (every 20 min). In recognition of the possibility that highly efficient photocatalytic surfaces may exhibit some diffusion control, the test notes that if  $\xi_{\text{MB}}$  is found to be >0.1%, the experiment should be repeated but with an irradiance of 0.25 mW/cm<sup>2</sup>. Although this approach appears a logical way to minimise the likelihood of an unwanted diffusion-controlled dependence on the calculated value of  $\xi_{\text{MB}}$  – it is flawed, since the kinetics of MB<sup>+</sup> photobleaching are highly dependent in a non-linear fashion, upon incident irradiance ( $I_0$ ), as described further in Section 3.5 [17,21]. Thus, reducing  $I_0$  from 1 mW/cm<sup>2</sup> to 0.25 mW/cm<sup>2</sup> will most likely produce an increase in  $\xi_{\text{MB}}$  even if  $\xi_{\text{MB}}$  is <0.1%.

As a consequence of the above, this test is, in effect, limited to application of fairly inactive films, for which  $\xi_{\text{MB}} \leq 0.1\%$ . It follows that any film which is able to fully bleach the MB<sup>+</sup> solution in less than ca. 110 min, as illustrated by the thick black line in Fig. 3, will generate a  $\xi_{\text{MB}}$  value >0.1% and so be deemed too reactive to provide a reliable value for  $\xi_{\text{MB}}$  using this test. If the ISO test system could be adapted so as to ensure the reaction is stirred, this limitation in application would not be so severe. In such cases, reliable values of  $\xi_{\text{MB}} > 0.1\%$  could be generated using stirrer speeds for which the value was found to be independent of stirrer rate. However, it is not obvious how this may be readily achieved with the standard's photoreactor (see Fig. 2) in its current format. A change of photoreactor with the sample on the side and a stirrer flea at the base, as illustrated in Fig. 5 is a possible alternative [22].

### 3.5. Mechanism

In the case of MB<sup>+</sup> the complete photomineralisation process by semiconductor photocatalysis (SPC) is summarised by the

following reaction equation:



However, it should also be recognised, when using a dye test system for assessing SPC activity, that dye photobleaching can also occur via a dye photosensitised process in which the electronically excited state of the dye, D\*, injects an electron into the conduction band of the semiconductor, SC, to produce an oxidised dye radical, D<sup>•+</sup>, which is unstable and able to decompose to form bleached products [18,23,24], i.e.:



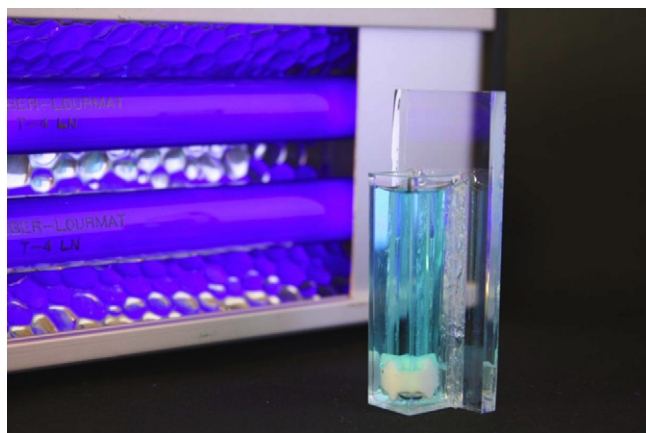
The injected electron can also promote this process via its subsequent reaction with O<sub>2</sub> to produce a number of different oxidising species, such as hydrogen peroxide.

It is usually possible to discriminate between dye bleaching caused by photocatalysis or dye-photosensitisation through the careful selection of the wavelength(s) of excitation [23]. Ideally, for measurements of photocatalyst activity, the wavelength of excitation should be such that the semiconductor alone is able to absorb the light. Fortunately, MB<sup>+</sup> has a minimum in its UV absorption spectrum around the wavelength of UV light usually used (i.e. 365 nm from a BLB lamp) for assessing the activity of UV-absorbing semiconductor photocatalysts such as TiO<sub>2</sub>, see Fig. 4.

Although this choice of light source minimises the risk that the observed photobleaching is due to reaction (3), it does not eliminate it and the component of the photobleaching rate due to reaction (3) will increase with increasing solution pathlength (measured from the top of the MB<sup>+</sup> solution to the surface of the sample, see Fig. 2). Thus, although the standard suggests that a solution height of 2–5 cm is appropriate, given the above concerns, this solution height should be fixed to the lowest suggested value, i.e. 2 cm, thereby fixing the cylinder internal diameter to 4.7 cm, given the solution volume is 35 ml.

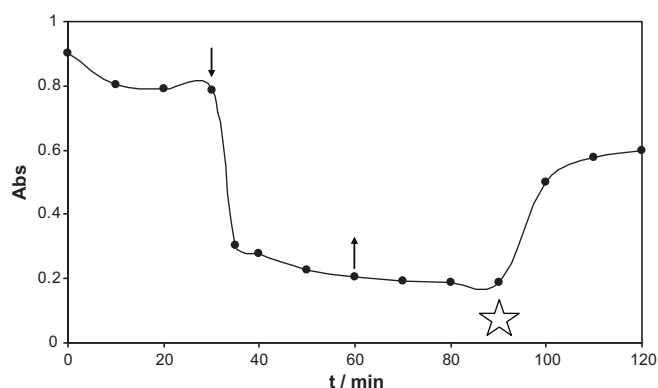
It is also clear that this standard, and possibly any dye-based test, is inappropriate for assessing the activity of visible light absorbing photocatalysts, using a visible light source; although it is appropriate for assessing the UV photocatalytic activity of a visible light absorbing photocatalyst using a UV (BLB) light source. A demonstration of the dominance of reaction (3) over reaction (2) in assessing the photocatalytic activity (reaction (2)) of a S-doped sample of titania using MB<sup>+</sup> and a visible light source has been elegantly demonstrated recently by Ohtani and co-workers [23].

Dye-sensitisation, i.e. reaction (3), is not the only alternative to photocatalytic mineralisation, reaction (2), whereby the photobleaching of MB<sup>+</sup> may be achieved. For example, in reaction (2) it is assumed that the photo-generated electron on the semiconductor photocatalyst (e<sup>-</sup>) is scavenged by dissolved oxygen, i.e.:



**Fig. 5.** Photograph of an alternative photoreactor system to that illustrated in Fig. 2. In the alternative photoreactor the sample is glued onto a plastic fluorescence cuvette to replace a removed optical face. This allows the sample to be stirred vigorously and continually using a crown stirrer flea and to be irradiated, perpendicular to the sample surface using light from BLB lamps which are here, for illustrative purposes, placed in the background.





**Fig. 6.** Absorbance (at 665 nm) of  $\text{MB}^+$  ( $10^{-5}$  M) in an oxygen-saturated, 10 mg dispersion of P25  $\text{TiO}_2$  in 100 ml of 0.01 M  $\text{HClO}_4$  as a function of time,  $t$ . At  $t = 30$  min, the system was irradiated with BLB UVA light ( $\downarrow$ ) and was fully bleached of colour by  $t = 60$  min, at which point ( $\uparrow$ ) the light was switched off and the system purged with  $\text{N}_2$ ; at  $t = 90$  min ( $\star$ ), the purge gas was changed to  $\text{O}_2$ .

And the photogenerated hole,  $h^+$ , oxidises the dye (either directly or indirectly) to eventually produce permanently bleached products, i.e.



In the presence of  $\text{MB}^+$  it appears likely that at pH's  $> 4$  reaction (4) is effectively catalysed by  $\text{MB}^+$ , since the latter is able to scavenge rapidly the photogenerated electrons via:



where: LMB is leuco-methylene blue (see Fig. 1), a colourless, reduced form of  $\text{MB}^+$ . LMB is known [25] to be oxidised very rapidly by oxygen at the pH  $> 4$ , i.e.



Thus, the combination of reactions (6) and (7) results in the effective catalysis of reaction (4) by  $\text{MB}^+$  at pH's  $> 4$ . The overall photocatalytic mineralisation of  $\text{MB}^+$ , via reactions (4) and (5), is increasingly favoured by rising solution pH values above 4.

However, if the local level of  $\text{O}_2$  is well below ambient (due to the very intermittent, i.e. poor, stirring recommended in the test, say) or the local pH of the  $\text{MB}^+$  solution at the film's surface, or in the bulk solution, was  $\ll \text{pH } 4$  (due acid contamination of the sample for example; note: the latter possibility is exacerbated by the fact that the present ISO test does not require any measurement of the initial pH) then the observed photobleaching of  $\text{MB}^+$  may be due in part to the photoreduction and simultaneous photooxidation of  $\text{MB}^+$ , i.e. reactions (6) and (5), with the concomitant oxidation of  $\text{MB}^+$ .

The above type of reaction,  $\text{MB}^+$  photobleaching, via a combined photoreductive and oxidative mechanism, is rather nicely illustrated in a study [26] of what is ostensibly the photocatalytic mineralisation of  $\text{MB}^+$  ( $10^{-5}$  M) in an oxygen-saturated, 10 mg dispersion of P25  $\text{TiO}_2$  in 100 ml of 0.01 M  $\text{HClO}_4$ . Some of the results of this study are illustrated in Fig. 6, and show that  $\text{MB}^+$  is bleached upon UVA irradiation, and that the reaction solution remains colourless when the irradiation light is turned off and the solution is at the same time purged with nitrogen, instead of oxygen. However, when the oxygen purge is reintroduced, into this now, non-illuminated, photobleached  $\text{MB}^+/\text{TiO}_2/\text{HClO}_4$  system, a substantial (68%) amount of the original colouration due to  $\text{MB}^+$  returns, due to reaction (7).

Obviously, it is preferable that the photobleaching of  $\text{MB}^+$  in the ISO standard experiment is due to reactions (4) and (5), i.e. due to the photocatalytic mineralisation of the dye. Fortunately,

there is a simple test for the contribution of the photoreductive-oxidative bleaching mechanism (reactions (6) and (5)) to the overall photobleaching process, namely: leaving the final photobleached reaction solution stirring and no longer irradiated (say overnight) under otherwise ambient conditions. Any observed recovery in dye colour, as measured by UV/vis absorption spectroscopy, will then identify the contribution of the photoreductive-oxidative bleaching mechanism to the overall photobleaching process. Only if no recovery in colour is observed would it be reasonable to assume that dye bleaching is mainly due to the photocatalytic bleaching of the dye, i.e. reaction (2), although some contribution to the bleaching process via the dye-sensitised photobleaching, reaction (3), cannot be completely or easily eliminated.

It could also be argued that the photobleaching of methylene blue could be achieved if the sample introduced a suitable sacrificial electron acceptor or donor species into the reaction solution that was able to quench the excited state of  $\text{MB}^+$ . Certainly  $\text{MB}^+$  has an efficiently generated (quantum yield = 0.52) and long-lived triplet state (4.5  $\mu\text{s}$ ) [27] that is able to effect the efficient photobleaching of  $\text{MB}^+$  by sacrificial electron acceptors or donors, such as hydrogen peroxide [28] or EDTA [29], respectively. However, the likelihood of such sacrificial species being present in the reaction solution at the necessary levels via contamination by the sample appears remote, unless, say, the film was formed from a colloid which used such species as stabilising or directing agents.

### 3.6. Reaction kinetics

The general initial kinetics of semiconductor photocatalysis usually give the appearance of being straightforward and are described by a simple equation which, for the photocatalytic bleaching of  $\text{MB}^+$ , would be as follows:

$$\frac{-d[\text{MB}^+]}{dt} = \frac{k_{\text{MAX}}K_L'[\text{MB}^+]}{1 + K_L'[\text{MB}^+]} \quad (8)$$

where,  $k_{\text{MAX}}$  is the maximum rate of  $\text{MB}^+$  observed at  $K_L'[\text{MB}^+]$  values  $\gg 1$  and  $K_L'$  is the apparent Langmuir adsorption coefficient. The system however is almost always much more complicated than Eq. (8) suggests, since the calculated value of  $k_{\text{MAX}}$  is dependent upon the incident light irradiance,  $I_0^\theta$ , where the value of  $\theta$  is unity at low irradiance levels, tending to 0.5 at high levels. The apparent Langmuir adsorption coefficient is rarely equal to the dark, Langmuir adsorption coefficient,  $K_L$ , but usually a much greater value than the latter AND also dependent upon  $I_0^\theta$ . A possible mechanism has been proposed recently which appears to account for these type of kinetics [30,31].

It was noted earlier that the ISO standard suggests lowering the irradiance level from 1 to 0.25  $\text{mW}/\text{cm}^2$  to see if a greater value of  $\xi_{\text{MB}}$  is generated when an initial value of  $\xi_{\text{MB}} > 0.1\%$ , is determined. If it remains the same, the standard implies the value of  $\xi_{\text{MB}}$  should be taken as being sound. From Eq. (8), however, it is clear that a greater value will almost always be expected at lower irradiance levels and so the exercise has little value! The complex dependence of the kinetics of reaction (2) upon  $I_0$  shows that it is essential that the irradiance used is fixed (1  $\text{mW}/\text{cm}^2$ ), and derived from a well-defined light source, such as a BLB

It also follows from Eq. (8) that the kinetics of photobleaching are highly, and not simply, dependent upon  $[\text{MB}^+]$  and so it is essential that the test is conducted using high purity  $\text{MB}^+$  at a fixed concentration, such as  $10^{-5}$  M (3.74  $\text{mg dm}^{-3}$ ) as suggested by the test. Given the variance in reported values for  $\epsilon_{\text{MB}}$  (see Table 1) it is hard to know what the absorbance of a such a solution at 665 nm in a 1 cm cell will be from one lab to another, i.e. from one supplier or batch to another. Thus, a more useful, practical approach, given the variance in purity of commercial samples, is to NOT specify

the concentration of MB<sup>+</sup>, but rather to specify its absorbance at 665 nm, such as 0.74 in a solvent-referenced 1 cm cell. This action will ensure that a fixed initial concentration of dye is used by all using the standard, even if the concentration of which is not exactly known (as it will depend upon the molar absorptivity used). If the molar absorptivity cited in the standard is used (74,028 M<sup>-1</sup> cm<sup>-1</sup>; [15]), the solution will have a nominal concentration of 10<sup>-5</sup> M.

Note that any deviation from the specified irradiance (1 mW/cm<sup>2</sup>) or dye concentration (suggested as Abs(665)=0.74, rather than the more error-inducing: 3.74 mg dm<sup>-3</sup>) would produce a different measured value for  $\xi_{\text{MB}}$  and so reduce the reliability and usefulness of the ISO standard, which is to allow the comparison of the photocatalytic activities of samples between laboratories across the world.

#### 4. Conclusions

The specified intended application of the ISO standard is for the assessment of photocatalytic self-cleaning products, whereas, as noted earlier, it appears more relevant to the use of such films for water purification. Why the commonly used destruction of stearic acid test has not been promoted as an ISO test for photocatalytic self-cleaning products remains unclear [32]. However, it seems likely that any measurement of the photocatalytic activity made using the MB<sup>+</sup> ISO standard will have relevance to its performance as a self-cleaning film.

In its present form the standard appears unlikely to yield particularly reliable values for  $\xi_{\text{MB}}$ , due to a number of weak underlying assumptions and poorly defined specifications. Evidence for the poor repeatability and reproducibility of the ISO standard as it stands is provided by the results of the inter-laboratory test conducted between 4 different German laboratories, reported in Annex C of the standard. These show that the specific photoactivity for MB<sup>+</sup> bleaching by the same film yielded *average* laboratory values ranging from: 14.9 to 26.9  $\mu\text{mol}/(\text{m}^2 \text{ h})$ ! A statistical analysis of the whole data set found the average percentage errors for repeatability (within a lab) and reproducibility (between labs) were 9.2% and 30.6%, respectively. Some of this significant degree of variance is due to the potential for error in the MB<sup>+</sup> ISO protocol due to a laxness in the definition of the reaction conditions and procedures.

A list of the changes suggested in this article to the ISO protocol which should improve markedly the reliability of the standard is as follows: (i) a source of MB<sup>+</sup> of known and proven on site high purity (>90%) should be used to make up the standard test solution, which should have a referenced absorbance = 0.74 at 665 nm; (ii) the conditioning solution should be the same concentration as the standard test solution, i.e. with an absorbance = 0.74 at 665 nm; (iii) the initial pH of the reaction solution should lie in the range: 5.5–6.0; (iv) the 1 mW/cm<sup>2</sup> UVA light used should be provided by a BLB source which uses a europium-doped strontium fluoroborate or borate phosphor and so generates an emission peak at ca. 365 nm with a 20 nm bandwidth; (v) the reaction solution should be vigorously and continuously stirred – this requirement most likely requires replacing the recommended photoreactor system illustrated in Fig. 2 with one that allows such stirring (such as illustrated in Fig. 5); (vi) if the photoreactor reported in the standard

(Fig. 2) is used, the solution height should be the minimum recommended value of 2 cm, and the cylinder i.d = 4.7 cm; (vii) after the 3 h irradiation the reaction solution should be left stirring overnight to provide a measure of the extent of colour recovery that occurs, as this will identify the degree of dye photoreductive bleaching that occurred; ideally the latter should be zero.

Fortunately, every ISO standard is reviewed after 3 years after publication, so it is possible to modify existing standards to embrace suggestions for improvements. The above suggested changes should improve the usefulness of the MB<sup>+</sup> ISO test and these and additional suggestions from other interested groups working in the field will eventually lead to a final, much improved and more valuable version which will go far in helping with new photocatalytic film development and commercialisation. Since the review of the current MB<sup>+</sup> ISO test will not take place until 2013 – it is worth considering employing the suggested improvements described above when using this test, especially as most involve the use of more closely defined reaction conditions and procedures (e.g. dye purity and concentration, UV lamp, pH, reaction solution height) than are currently given in the existing standard. Their application should improve markedly the repeatability, reproducibility and usefulness of the existing MB<sup>+</sup> ISO standard.

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